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TRANSVERSE COLLECTIVE ATOMIC VIBRATIONS IN LIQUID LEAD

P. D. Randolph and W. R. Myers

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IDAHO NUCLEAR CORPORATION

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ABSTRACT

Slow neutron inelastic scattering measurements have been made of the dispersion relations $\omega(\kappa)$ for the collective vibrational modes in liquid lead at 350°C, for small scattering angles (3° to 18°) at incident energies of 30 and 50 meV. The collective excitations appear as abrupt slope changes or shoulders in the energy spectra of inelastically scattered neutrons and span momentum transfers $h\kappa$ in the range of $0.3 \leq \omega \leq 1.5 \text{ \AA}^{-1}$ and frequencies $1.5 \leq \omega \leq 15 \times 10^{12} \text{ rad/sec}$. Usually two such excitations occur at a given scattering angle and sometimes three. The data show that three modes of collective vibrations exist similar to longitudinal and transverse acoustic vibrations in the solid, but the branches cannot be clearly distinguished over the whole κ range. A lower limit for the transverse relaxation time is estimated and it is concluded that for times of the order of 10^{-12} sec the groups of atoms supporting the modes are not isotropic.

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INTRODUCTION

Recently slow neutron inelastic scattering experiments have shown the existence of high frequency ($\omega \sim 10^{13}$ rad/sec) collective modes of atomic vibrations in liquid lead^(1,2) and tin⁽²⁾. Such modes have also been observed in liquid Ne, Ar, D₂ and CF₄⁽³⁾. These modes, which appear as broad peaks or shoulders in the spectra of inelastically scattered neutrons, are short lived ($\sim 10^{-12}$ sec) and highly damped. The most extensive data of this kind is for liquid lead at 350-360°C, and a plot of frequency vs. wave vector $\omega(\kappa)$ for liquid lead shows a well defined dispersion "band" (rather than a curve) between $1.2 \leq \kappa \leq 2.2 \text{ \AA}^{-1}$. The origin of this band is at $\kappa \approx \kappa_0 = 2.2 \text{ \AA}^{-1}$ which is the position of the first maximum in the static structure factor $S(\kappa)$, i.e. the diffraction pattern. The shape and slope of this band is in agreement with the longitudinal acoustical branches observed in single crystal lead⁽⁴⁾. A more recent experiment⁽⁵⁾ has confirmed this dispersion band and extended the measurements to $\kappa = 3.0 \text{ \AA}^{-1}$, showing that this band, similar in slope and shape to a longitudinal branch, exists symmetrically on both sides of κ_0 . The existence of this dispersion relation for κ values both larger and smaller than κ_0 supports the hypothesis that there exist at least two "quasi-Brillouin zones" in liquid lead. The first zone is centered at $\kappa = 0$, and the second is centered at κ_0 , but the center is smeared out rather than a point since there is no long range order present.

In the first quasi-Brillouin zone below $\kappa \approx 1.2 \text{ \AA}^{-1}$ the data are sparse, and show anomalous behavior if it is assumed that only a longitudinal mode exists. We report here on a neutron scattering experiment to obtain further information on the collective modes of liquid lead in the first quasi-Brillouin zone. Our results extend the measurements in this region and show that rather than an anomalously longitudinal band, at least three acoustical dispersion bands exist.

EXPERIMENT

The experiment was performed using the MTR phased chopper velocity selector. Data were taken at incident energies of 49.5 meV and 29.8 meV. Simultaneous scattered neutron spectra were obtained at 12 scattering angles between 3° and 18° . The sample, the neutron flight paths and the detectors were all contained in an evacuated flight path. Each detector bank consisted of 2 six inch active-length He^3 counters one inch in diameter located 2.26 m from the sample. The sample was in the form of a rectangular slab 0.127 cm thick contained between windows of 0.049 cm molybdenum. It was maintained at $350^\circ \pm 5^\circ\text{C}$ and the temperature monitored continuously with a recorder⁽⁶⁾. An identical empty sample holder was used to measure the background scattering. The measured sample transmission at 0.0298 eV was 0.94. After correction for background contributions and detector efficiency the time of flight spectra at each angle were converted to the energy cross section, $\frac{d^2\sigma}{d\Omega dE}$ vs. scattered neutron energy⁽⁷⁾.

Figures 1 and 2 show representative plots of these spectra taken at each incident energy. The energy resolution is also shown. The κ region we are concerned with is well below κ_0 , the first maximum in the

structure factor $S(\kappa)$, and counting rates are very low. Also at these κ values, measurements of the first moment of the energy-transfer⁽⁵⁾ show that there are relatively large multiple inelastic scattering contributions which tend to obscure the excitations of interest. The spectra shown in Figures 1 and 2 generally have only a single maximum, and with few exceptions, the quasi-elastic scattering cannot be clearly separated from the broad spectrum of inelastic scattering. The inelastic scattering is marked by abrupt slope changes or shoulders. These shoulders (see arrows) are due to excitation of the collective modes in the liquid and occur in the "first quasi-Brillouin zone" wherever the curve of constant scattering angle in ω - κ space crosses the dispersion relation $\omega(q)$, (q is the wave vector of the excitation). The most striking feature of these spectra is the appearance of more than one such excitation, usually in the energy loss side of the spectrum. This is most noticeable at the larger scattering angles where the slope changes can be clearly separated from the quasi-elastic contribution. At the smallest angle no quasi-elastic peak is observed and only two inelastic peaks are seen, one in neutron energy gain and one in energy loss. In the case of the 30 meV data, Figure 2, the positions of the two well defined inelastic peaks at 3.08° are not marked with arrows. The peaks are indeed excitations of interest but were not used due to an uncertainty in the background correction. This uncertainty arose from the small incoherent elastic peak caused by the molybdenum windows of the sample holders. As the angle increases, the quasi-elastic contribution increases, and this together with the shoulders at small energy change cause a rather flat topped maximum. At the larger angles as the structure factor becomes larger the quasi-elastic

peak stands out more clearly. In the 30 meV data at scattering angles of 11.24° and 12.65° three such shoulders are present on the energy loss side of the spectra.

DISCUSSION

It is clear therefore that three modes of collective excitation exist in the liquid; but, over most of the κ range of the experiment, only two can be distinguished at a given angle. One of the modes is longitudinal; and presumably the two lower frequency modes are transverse in character. These lower frequency modes are, of course, not purely transverse. As has been shown by Larsson⁽⁸⁾ the liquid metal spectra are very similar to those of the polycrystalline solid. In analogy with the solid, in the first "Brillouin zone" where $\vec{\kappa} = \vec{q}$, the polarization factor $(\vec{\kappa} \cdot \vec{\xi})^2$ which governs the intensity of one-phonon coherent scattering ($\vec{\xi}$ is the polarization vector of the phonon) allows observation of only the longitudinal component of a collective excitation. What is observed therefore is the longitudinal component of the primarily transverse modes, integrated over all directions of the quasi-phonon wave vector $\vec{q}$. Generally, no separation of modes can be made and a given shoulder may contain contributions from more than one mode.

Figure 2 shows the $\omega(\kappa)$ plots for this experiment together with earlier results. The positions of the shoulders for both neutron energy gain and loss were used. Also shown (dotted) are the solid lead phonon dispersion curves⁽⁴⁾ in the three symmetry directions $[\xi 0 0]$, $[0 \xi 0]$ and $[\xi \xi \xi]$. The upper three dotted curves are longitudinal branches and the remaining four are transverse. The flags are estimates

of the error in our ability to locate the shoulders in the spectra and amount usually to one time of flight channel, except at the lower values of E (larger ΔE) where the time of flight channels are more closely spaced on an energy scale. The points labeled A, B correspond to three energy loss excitations observed in the 30 meV data at 11.29° and 12.65° respectively. The data, with a few exceptions at high frequency, lie well in the region one would expect from the single crystal measurements. It is also in agreement with previous data; in particular the low κ points of Dorner et al⁽¹⁾ and Cocking and Egelstaff are confirmed. Three collective modes exist but no unambiguous distinction between modes can be made over the whole κ range. If it is assumed that all modes are acoustical, then below $1 \text{ \AA}^{-1}$ there is a fairly well defined low frequency dispersion band that follows the two lowest frequency transverse acoustical modes of the solid. If the two upper transverse solid lead curves are used as a guide, there is a possible but not unique band lying between the curves. Above this would be the longitudinal band.

The above discussion has been based on the assumption that all the excitations are acoustical vibrations, however this experiment does not rule out the possible existence of optical modes. The points at $\omega \approx 1.4 \times 10^{12}$ which lie above the longitudinal branches for a solid could be due to optical excitation. Because of experimental limitations on the scattering angles we are not able to make observations in the region $\omega > 10 \times 10^{12}$, $\kappa < 0.5 \text{ \AA}^{-1}$ which would decide whether there is an optical band. If, as is reasonable, we assume that the observed excitations are primarily due to acoustic modes then the lack of distinguishable bands or branches implies that the

dispersion relation depends on the direction of the wave vector q . That is, the experiment samples all directions of $\vec{q}$ at any fixed $|\vec{k}|$ and a variation of $\omega(\vec{q})$ as $\vec{q}$ changes direction smears out the band. A dependence of $\omega(\vec{q})$ on the direction of q means that on the time scale of observation ($\sim 10^{-12}$ sec) the groups of atoms that maintain sufficient order to support the collective modes are not isotropic. Rahman⁽⁹⁾ has reached a similar conclusion in his computer studies of the pair density function for liquid argon. One more point can be made; it is estimated from the lowest observed frequency of transverse vibration ($\omega \approx 1.5 \times 10^{12}$) that a lower limit on the shear relaxation time τ is $\tau \geq \frac{1}{\omega} = 0.66 \times 10^{-12}$ sec.

SUMMARY

- A) In the first "quasi-Brillouin zone" of liquid lead 3 modes of collective excitations exist, but are very smeared out and cannot be unambiguously separated.
- B) The modes are predominantly acoustical in nature, but the possibility of optical modes is not precluded. One branch approximates the longitudinal branches of the solid, and the others are by analogy the primarily transverse modes.
- C) On the short time scale of observation the atomic arrangement supporting the vibrations is not isotropic.
- D) The shear relaxation time in the liquid is $\geq 0.7 \times 10^{-12}$ sec.

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6. After heating the sample to an indicated temperature of 350°C, but prior to evacuating the scattering chamber, a wire probe inserted through a hole at the top of the sample holder determined that the sample was actually a liquid.
7. In the case of the 30 meV data a bipolar average of the raw data was done to reduce fluctuations caused by poor counting statistics, i.e. $(N_i)_{Av} = \frac{1}{2} [N_{i-1} + N_{i+1}]$ where N_i is the background corrected counts in the i th time of flight channel. This was not done for the 50 meV data.
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1. Scattered neutron energy spectra for liquid lead at 49.5 meV incident energy. The arrows mark the energies assigned to the excitation of "quasi-phonons".

2. Scattered neutron energy spectra for liquid lead at 29.8 meV incident energy. Arrows mark the energies assigned to the excitations of "quasi-phonons". Note that three such excitations appear in neutron energy loss at 11.29° and 12.65°.

3. Dispersion relations for liquid lead at 350°C.